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DUAL PHOTOREACTIONS OF PHTHALAZINE FROM THE LOWEST EXCITED SINGLET AND TRIPLET STATES

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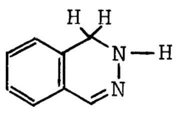
Phthalazine undergoes the photoreduction and the photo-reductive dimerization simultaneously to give 1,2-dihydrophthalazine and its dimer (1*H*,1'*H*,2*H*,2'*H*-1,1'-biphthalazine), respectively, upon ultraviolet light irradiation in 2-propanol. It has been suggested that the photoreduction proceeds through the lowest excited singlet state and the photodimerization through the lowest triplet state.

There are not many descriptions concerning the photochemistry of phthalazine. Previously Wake et al.[1)] reported that phthalazine underwent the photoalkylation upon irradiation in acidified alcohols and that the reductive dimerization product was obtained upon irradiation in 2-propanol without added acid. Hitherto, however, little is known about photochemical reactions of phthalazine especially in neutral solvents. Here we wish to report on the photoreactions in alcoholic solvents.

The absorption spectral change with elapse of UV irradiation time is shown in Fig.1 for a 2-propanol solution of phthalazine. At the initial stage of the reaction, the absorption band appeared at 340 nm. With successive irradiation the absorption maximum was shifted progressively to shorter wavelength accompanying the increase in intensity, and finally the absorption maximum appeared at 315 nm. Work-up of the irradiated solution gave two photoproducts[2)]; one(1) having the bands at 315 nm and 232 nm and the other(2) having the bands at 340 nm and 243 nm. The products 1 and 2 were identified as 1,2-dihydrophthalazine and its dimer (1*H*,1'*H*,2*H*,2'*H*-1,1'-biphthalazine), respectively.[2)]



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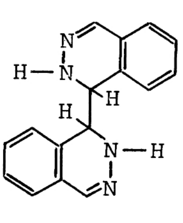

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Using the molar absorption coefficients of 1 (ε_{315nm}=388 m^2 mol^{-1}) and 2 (ε_{340nm} =629 m^2 mol^{-1}), the changes in the concentrations of 1 and 2 during the course of the reactions were determined as illustrated in Fig.2. The amount of 1 produced gradually increased with the irradiation time (37% yield for 140 min irradiation), whereas the amount of 2 reached a constant value (40% yield based on the starting material) after appropriate time of the irradiation, although 2 was produced more rapidly than 1 in the initial stage of the reaction. These results could be interpreted as indicating that 2 is formed first and then decomposed to 1. However, this is not the case. Irradiation of 366 nm light on a 2-propanol solution of isolated 2 resulted in the photodecomposition yielding phthalazine almost quantitatively.3) Therefore, the saturation of 2 in the course of the reaction (curve 2 in Fig.2) can be attributed to this backward photoreaction, and phthalazine and 2 are in the photostationary state after sufficient irradiation time. On the other hand, 1 does not undergo a pronounced photoreaction.4)

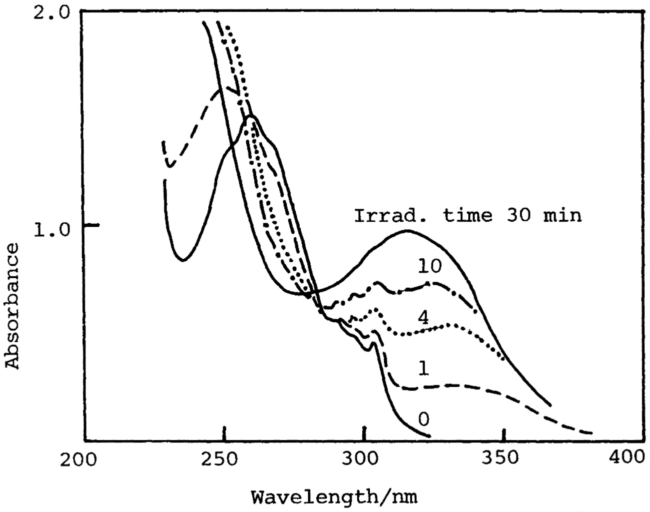

Fig.1. Spectral change caused by UV irradiation (low-pressure Hg lamp) of phthalazine in 2-propanol (4.0×10^{-4} mol dm^{-3}).

The quantum yields for the product formations were determined for 2-propanol solution at the initial stage of the reactions as to be $\Phi(1)=0.013$ and $\Phi(2)=0.040$. Both of these values were not affected by the change in the concentration of the reactant in the range of 2×10^{-4}– 1×10^{-3} mol dm^{-3}. Moreover, temperature dependence was not noted in the range of 7–58 °C. From these observations plausible mechanism that 2 is formed from 1 can be discarded. Consequently, it is evident that 1 and 2 are formed independently and the interconversion between them can be ruled out as reaction mechanism.

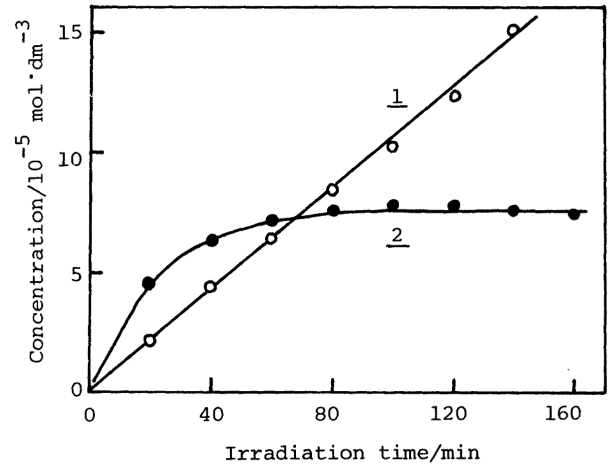

Fig.2. Change in the concentrations of the products 1 and 2 with UV irradiation (low-pressure Hg lamp) of phthalazine in 2-propanol (4.0×10^{-4} mol dm^{-3}).

In order to elucidate the reactive states for the respective photoreactions, quenching experiments were performed using 2,4-hexadien-1-ol as a triplet quencher whose triplet energy (249 kJ mol^{-1})5) is lower than that of phthalazine (256 kJ mol^{-1}).6) The results are presented in Fig.3, in which the Stern-Volmer quenching plots for both reaction quantum yields are illustrated. The formation of 2 is apparently quenched, while the formation of 1 is not influenced by the addition of the quencher up to 1.0×10^{-3} mol dm^{-3}. The quenching for the phosphorescence (480 nm) of the substrate in a mixture of ethanol and methanol (1:1) at 77 K is also observed in the presence of the same quencher as shown in Fig.4.7) It has been confirmed that the intensity and the shape of the absorption and the shape of the phosphorescence spectra are not altered by the quencher. This implies that there

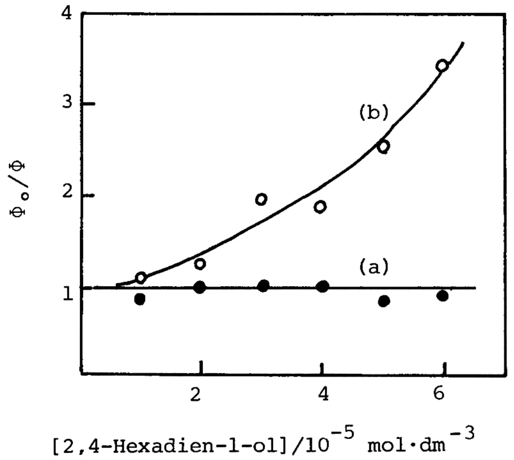

Fig.3. Stern-Volmer quenching plots for the quantum yields of the formation of 1 (a) and the formation of 2 (b). [phthalazine]=2.0X10^{-4} mol dm^{-3}. Excitation wavelength: 313 nm.

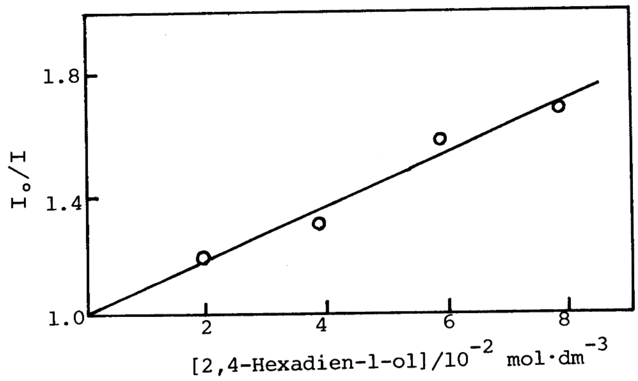

Fig.4. Stern-Volmer quenching plots for the phosphorescence of phthalazine at 77 K. [phthalazine]=1.0X10^{-3} mol dm^{-3}. Excitation wavelength: 313 nm.

is no special interaction between the substrate in the ground and the lowest triplet states and the quencher.[8)] Any reaction of the products 1 and 2 with the quencher could not be observed. Therefore, the quenching observed for the formation of 2 can be interpreted in terms of the triplet-triplet energy transfer. Since S_1 of phthalazine is lower than that of the quencher,[9)] the singlet energy transfer from the substrate to the quencher is impossible in the present system.

Furthermore, triplet sensitization for the formation of 2 by 4,4'-bis(dimethylamino)benzophenone (Michler's ketone, E_T=259 kJ mol^{-1}) was observed using 366 nm light which was absorbed only by the sensitizer, whereas the formation of 1 was not sensitized by this compound.

The results obtained here lead us to propose the reaction mechanism that 1 is formed from the S_1 state of the substrate and 2 from the T_1 state. According to this mechanism, sufficient S_1– T_1 intersystem crossing yield is required for the relatively higher quantum yield of the formation of 2 described above. In this connection, triplet quantum yield (Φ_{ISC}) at room temperature was reported earlier as to be 0.43.[10)]

In contrast to the photoalkylation in which the initial step is proposed to be electron-transfer from solvent to excited phthalazine in acidified alcohol,[1)] both photoreactions presented here can be considered to be initiated by hydrogen-abstraction, because methanol is not good solvent. This is in accordance with the mechanism of the photoreductions of other azaaromatic compounds in the absence of acid.[11)]

The study on the detailed mechanism is in progress.

References

1) S.Wake, Y.Takayama, Y.Otsuji, and E.Imoto, Bull. Chem. Soc. Jpn., 47, 1257 (1974).

2) *Isolation and Identification of* 1. A 3X10^{-3} mol dm^{-3} solution of phthalazine

in 500 cm^3 of 2-propanol was irradiated for 5 h using a high-pressure mercury lamp under nitrogen. The irradiated solution was evaporated to dryness and the residue was subjected to TLC (silica gel, chloroform-methanol 30:1). The compound thus obtained showed the following properties: IR(KBr) 3250(NH) 1440 cm^{-1}(CH_2); ^1H NMR($CDCl_3$) δ 4.2(2H,s,CH_2), 5.3(1H,m,NH), 6.8-7.6(5H,m,aromatic H); mp 62.5-64.0 °C(decomp.). The product 1 was identified as 1,2-dihydrophthalazine. Further supporting evidence for the identification of 1 was obtained from the benzoyl derivative of the isolated product. Treatment of the product with *p*-methylbenzoylchloride gave the benzoyl derivative which was characterized by IR and elementary analysis.

Isolation and Identification of 2. A 1.5×10^{-2} mol dm^{-3} solution of phthalazine in 500 cm^3 of 2-propanol was irradiated for 8 h using a low-pressure mercury lamp under nitrogen. The irradiated solution was concentrated under reduced pressure. The crystals precipitated were collected by filtration and recrystallized twice from methanol. The physical properties of these crystals were identical with those of the reductive dimerization product reported by Wake et al.[1)] The product 2 was identified as 1*H*,1'*H*,2*H*,2'*H*-1,1'-biphthalazine.

3) Because 2 has the absorption band at longer wavelengths than phthalazine, the selective excitation of 2 can be performed with 366 nm light without the excitation of phthalazine produced. Detailed study on the mechanism of the photolysis of 2 is in progress.

4) Irradiation of 313 nm light on a solution of 1 causes photolysis very slowly to give unidentified product(s).

5) S.L.Murov, "Handbook of Photochemistry," Marcel Dekker, Inc., New York (1973), p.4.

6) H.Rau, Ber. Bunsenges. Phys. Chem., 72, 408 (1968).

7) In the case of the phosphorescence quenching, the concentrations of the quencher are relatively high compared with the case of the reaction (Fig.3), because of poor fluidity of the low temperature glass (a mixture of ethanol and methanol 1:1). The feature of the phosphorescence quenching plot differs from that of the reaction (Fig.3). Discussion on this respect will be made elsewhere on the basis of the T_1-T_2 separation.

8) Since phthalazine emits no fluorescence, interactions in the S_1 state can not be observed.

9) Although the energy of the lowest excited singlet state of 2,4-hexadien-1-ol is not known, it is evident from the absorption spectra that it is higher than that of phthalazine.

10) D.W.Boldridge, G.W.Scott, and T.A.Spiglanin, J. Phys. Chem., 86, 1976 (1982).

11) F.R.Stermitz, C.C.Wei, and C.M.O'Donnell, J. Am. Chem. Soc., 92, (1970), and references cited therein.

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